AD-A135 656 CYCLIC AND HIGH POLYMERIC PHOSPHAZENES AS CARRIER MOLECULES FOR CARBORANY..(U) PENNSYLVANIA STATE UNIV UNIVERSITY PARK DEPT OF CHEMISTRY H R ALLCOCK

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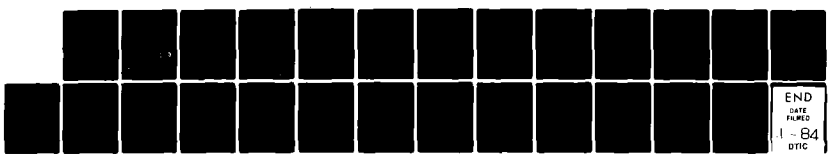

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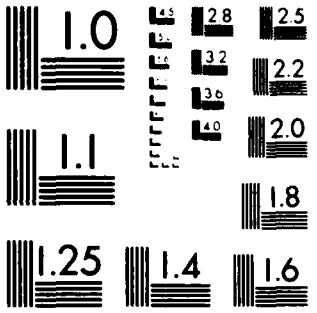

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Cyclic and High Polymeric Phosphazenes as Carrier Molecules for Carboranyl, Metallo, or Bioactive Side Groups

by

Harry R. Allcock

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University Park, Pennsylvania

December 5, 1983

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CYCLIC AND HIGH POLYMERIC PHOSPHAZENES AS CARRIER MOLECULES FOR CARBORANYL, METALLO, OR BIOACTIVE SIDE GROUPS

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Cyclic and high polymeric phosphazenes can be modified by nucleophilic-type substitution reactions to generate a wide range of derivatives. Recent developments include the introduction of bioactive organic residues to yield biologically-active high polymers and the synthesis of transition metal derivatives of phosphazenes. In addition, hybrid phosphazene-carborane compounds have been prepared including examples in which nido-carboranyl units, attached to a phosphazene ring or chain, function as binding sites for transition metal organometallic units.

Most inorganic research involves work with small molecules, and relatively little concentrated effort has been devoted to the macromolecular aspects of the subject. The complexity of the macromolecular chemistry has undoubtedly contributed to this neglect. However, it is clear from recent work that dramatic advances in both fundamental science and technology would be possible if the high polymer chemistry of the representative elements were to be studied in detail. Indeed, the much-heralded renaissance in Main Group chemistry may ultimately depend on a closer investigation of the macromolecular aspects of the field.

My purpose here is to illustrate what can be accomplished with just one inorganic macromolecular system -- in this case constructed from a backbone of phosphorus and nitrogen atoms. Almost certainly, other systems based on the Main Group elements can be developed to an equal or greater degree. I hope that the following comments will stimulate an increased interest in that direction. I will also attempt to illustrate the relationship between the fundamental chemistry on the one hand, and an approach to solving practical problems on the other.

Guiding Principles

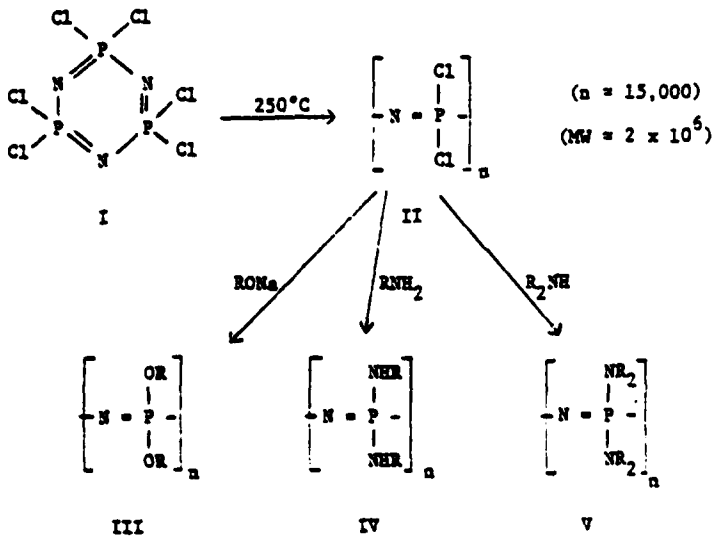
Nearly all synthetic polymers are synthesized by the polymerization or copolymerization of different "monomers." The chain growth process may involve the addition chain reactions of unsaturated small molecules, condensation reactions, or ring-opening chain-coupling processes. In conventional polymer chemistry, the synthesis of a new polymer requires the use of a new monomer. This approach is often unsatisfactory for inorganic systems, where relatively few monomers or cyclic oligomers can be induced to polymerize, at least under conditions that have been studied to date. The main exception to this rule is the condensation-type growth that occurs with inorganic di-hydroxy acids.

Because the opportunities for controlled chain growth are more restricted in inorganic than in organic systems, an alternative approach to polymer synthesis becomes appealing. This involves the use of substitution processes carried out on a preformed reactive polymeric intermediate. In this way molecular diversity can be introduced by different substitution reactions rather than by a diversification of the polymerization process.

If this principle can be applied, two potential problems must be avoided: the substitution reactions must lead to neither chain cleavage nor crosslinking.

Simple Substitution Reactions with Poly(dihalophosphazenes)

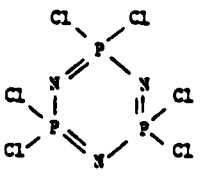
Poly(dichlorophosphazene) (II) is a highly reactive inorganic macromolecule. It can be prepared by the carefully controlled thermal polymerization of the cyclic trimer, hexachlorocyclotriphosphazene (I), itself synthesized from phosphorus pentachloride and ammonium chloride. In solution, the chlorine atoms in II can be replaced readily by reaction with a wide variety of organic nucleophiles (1,2,3) (Scheme 1). The resultant polymers (III-V) are stable and display a range of physical and chemical properties determined by the nature of the organic side groups. This synthesis process has been reviewed in detail elsewhere (4-7). Here it is sufficient to note that several hundred poly(organophosphazenes) have been prepared by this method. Polymers of this type are already being used in technology; they are also of considerable scientific interest. Similar syntheses have been developed based on poly(difluorophosphazene), $(NPF_2)_n$ (8).



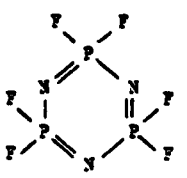
Scheme 1

Cyclic Trimers and Tetramers as Reaction Models

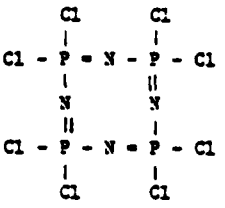
From a theoretical and mechanistic point of view, small molecule rings are much easier to study than long macromolecular chains. Substitution reactions carried out on macromolecular substrates may involve side reactions that lead to chain cleavage or crosslinking. Mechanistic studies with macromolecules are difficult to carry out because of solution viscosity effects, distributions in chain length, and the problems of characterization. Hence, it is prudent to explore potential new reactions first with the use of small molecule models such as I, VI, and VII and then to extend these reactions to the high polymers.



I



VI



VII

Some of the polymeric reactions mentioned below are still under study at the model compound level.

Modern Objectives in Polymer Synthesis

Polymers have been valued since antiquity for their solid state properties. By this is meant their ability to undergo chain entanglement or co-linear orientation and microcrystallization in the solid state. This underlies their use as structural materials, films, fibers, and elastomers. Such properties still constitute the driving force for most polymer-oriented research, especially with respect to the synthesis of heat-stable, radiation-stable, or highly flexible materials. The electrical properties of solid polymers have always been of interest.

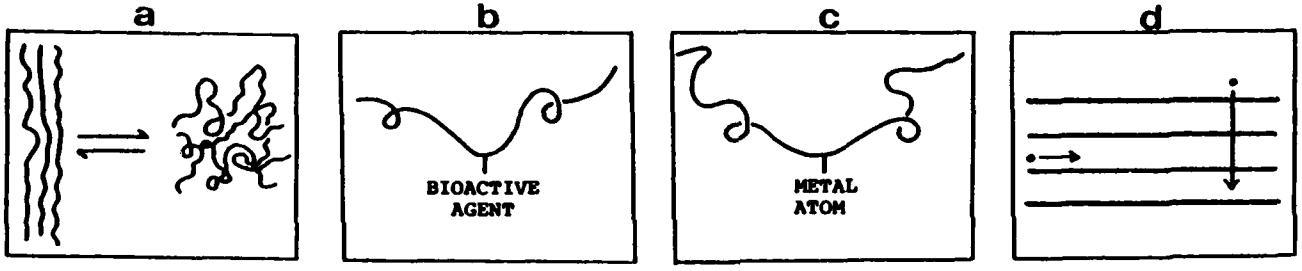
However, in recent years another approach to polymer chemistry has received increased emphasis. In this, macromolecules are studied in terms of their behavior as single molecules rather than as molecular conglomerates. In solution, polymer molecules behave differently from small molecules because the long chain length permits extensive coiling, reduced translational mobility, and an inability to pass through semipermeable membranes. Lightly crosslinked polymers behave like linear polymers in solution except that the swollen matrix has a physical immobility and an open matrix character unlike any other system. For these reasons, polymers are of great interest as "carrier molecules" for chemotherapeutic drugs or transition metal catalysts.

Finally, single macromolecules, because of their one-dimensional character, offer the promise of sequential side group coding, information storage, and template function in the manner that is well known in biological polymers (Figure 1).

Conventional synthetic organic polymers are being studied for all of these reasons, but the general lack of chemical reactivity in these systems is a serious drawback. It is for this reason that polyphosphazenes, with their substitutive

Figure 1

TRADITIONAL AND EXPLORATORY USES FOR MACROMOLECULES

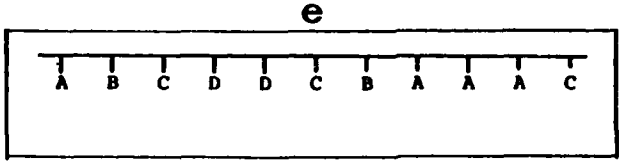


HIGH TECHNOLOGY POLYMERS

BIOACTIVE POLYMERS. MODELS FOR BIO-POLYMERS

INFLUENCE OF MACRO-MOLECULES ON CATALYSIS

ELECTRICAL CONDUCTORS OR SEMICONDUCTORS



SELF-ASSEMBLING STRUCTURES. TEMPLATES. INFORMATION STORAGE

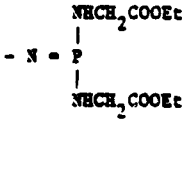
method of synthesis, are of considerable interest. In the following sections, I will illustrate why the polyphosphazene system is an appealing starting point for new developments in two specific areas -- in chemotherapy and polymer-bound catalyst work.

Bioactive Polyphosphazenes

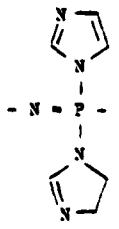
Specific inorganic macromolecules are unusual because they can be hydrolyzed to relatively innocuous products or to small molecules that can be metabolized. Most conventional organic polymers do not have this attribute. Thus, these inorganic systems are of special interest as carrier molecules in chemotherapy.

Recent work in our laboratory has shown that certain side groups attached to a polyphosphazene chain impart a sensitivity to hydrolytic chain cleavage; other side groups generate water-solubility. Both of these characteristics are important in chemotherapy. Polyphosphazenes are also valuable in biology because two or more substituted groups can be readily attached to the same chain. Thus, individual side groups that possess chemotherapeutic, water-solubilization, hydrolytic-destabilization, or "homing" characteristics can be combined in one molecule to form a drug with a set of synergistic properties.

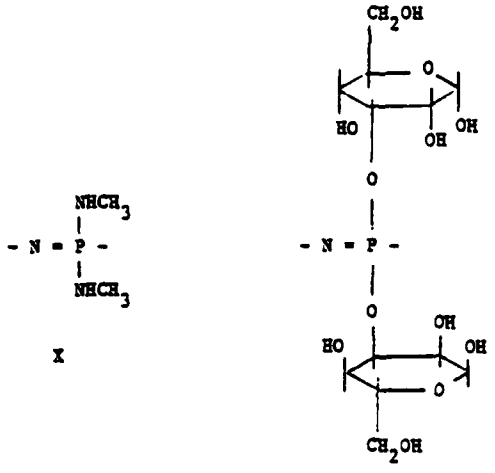
Polymers containing the repeating units shown in VIII-XI have been shown to be hydrolytically degradable and/or water-soluble (9-13). Amino acid ester derivatives (VIII) degrade to ethanol, amino acid, phosphate, and ammonia, which can either be metabolized or excreted. Thus, such side units used together with chemotherapeutic cosubstituent groups, provide a facile drug delivery system. Imidazolyl side groups (IX) also confer hydrolytic sensitivity, but the biochemical response to the hydrolysis products has not yet been established. Methylamino side groups (X) provide water-solubility, as do glucose residues (XI).



VIII



IX

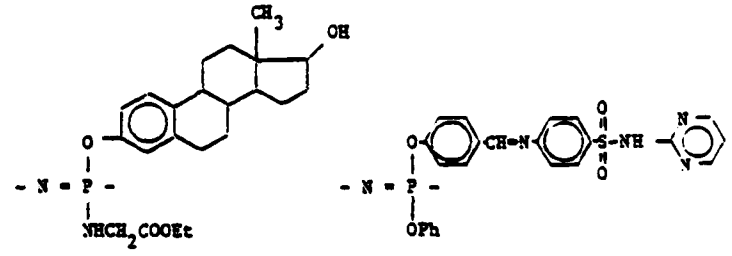


X

XI

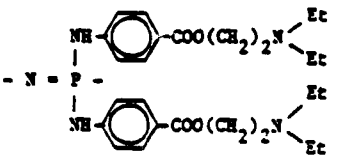
These polymers were synthesized by the general methods shown in Scheme 1. Their hydrolysis behavior has been the subject of several fundamental mechanistic studies at the model compound level (10,11).

The attachment of biologically-active side groups has also been explored. At the present time several different approaches have been developed which lead to the synthesis of polymers such as XII-XVII.

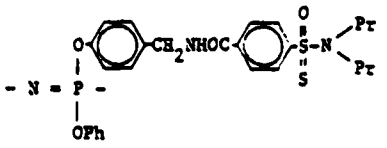


XII

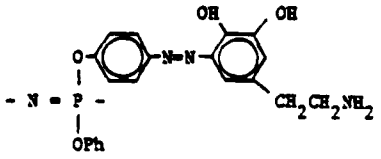
XIII



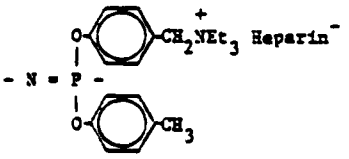
XIV



XV



XVI



XVII

Steroid-bound polyphosphazenes (XII) can be prepared by the reaction of II with metal steroidoxide salts followed by treatment with amino acid esters (14,15). The sulfadiazine-bound polymer (XIII) was synthesized by Schiff's base coupling of a polyphosphazene bearing a pendent aldehydic group with the antiobiotic amine (16). The local anesthetic, procaine, was linked to the polymer backbone by direct aminolysis of II to yield polymers based on the repeating unit XIV (17). Peptide-coupling techniques have been used for the linkage of polyphosphazenes bearing pendent amino residues to bioactive carboxylic acids (XV) (18). Catecholamines, such as dopamine or epinephrine, have been linked to aryloxyphosphazene high polymers by diazo coupling methods (XVI) (19), and these polymers retain the biological activity of the free hormone. The mucopolysaccharide, heparin, can be bound to aryloxyphosphazene polymers via ionic exchange

with quaternized ammonium pendent groups (XVII) (20). These polymers show promise as non-thrombogenic materials for bio-engineering.

It will be clear that, combined with the use of hydrolytically-sensitizing or water-solubilizing cosubstituent groups, these polymers could have an important impact on chemother ·v and other areas of biomedicine. At present, the problem is establish the feasibility of a wide range of synthetic me· is and to evaluate the biological activity of each class of mers.

Linkage of Transition Metals to Phosphazene Rings and Hig Polymers

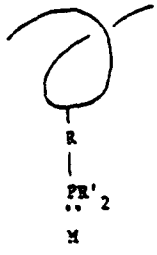
This book comprises a survey of recent advances in t chemistry of the representative (Main Group) elements. , the long-range resurgence of Main Group chemistry as an expanding research area depends to some extent on the strength of its interface with organic chemistry, transition metal chemistry, and applied science. Some organic-related aspects of phosphazene chemistry were discussed in the previous section. Here the interface with transition metal chemistry is reviewed.

Polyphosphazenes and cyclophosphazenes are almost unique as carrier molecules for transition metals because of the wide range of binding sites that can be incorporated into the phosphazene structure. The substitutive mode of synthesis described earlier allows a structural diversity that is not found, for example, in polystyrene, polyphenylene oxide, or other organic carrier polymers.

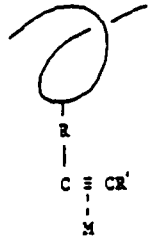
The emphasis in the following sections will be on exploratory model reactions carried out with phosphazene cyclic trimers or tetramers, although the analogous macromolecules systems have also been studied in several cases. First, I will summarize the various types of metal binding sites that are accessible at the present time. Synthetic procedures leading to the incorporation of several of these sites and their role in metal binding will then be discussed.

Options for Metal-Binding Sites. Seven approaches for metal-binding to cyclic or polymeric phosphazenes have been explored in our laboratory. These are summarized in structures XVIII (21), XIX (22-25), XX (26), XXI (27), XXII (28,29), XXIII (30), and XXIV (31,32,33).

XVIII



XIX



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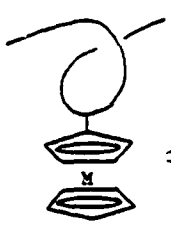
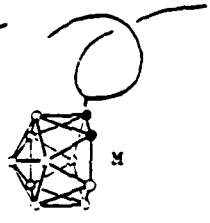
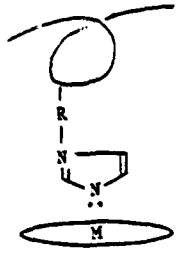


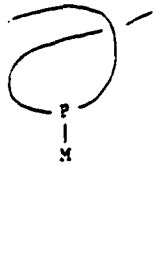
XXI



XXII



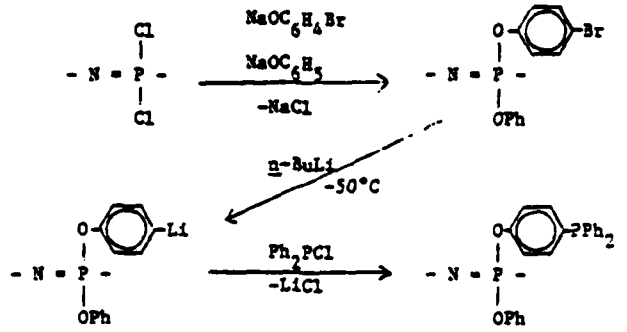
XXIII



XXIV

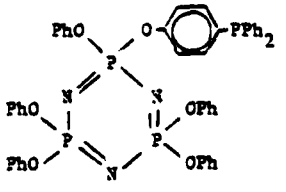
Only three of these approaches will be discussed here. The others can be traced through the references given.

Pendent Phosphine Groups. The classical method for the linkage of transition metal units to high polymers is via pendent phosphine groups attached to a macromolecular chain. We have developed a synthetic strategy for the preparation of cyclophosphazene model compounds and the corresponding linear high polymers which bear pendent triarylphosphine groups. This approach is illustrated in Scheme 2 (22-25).

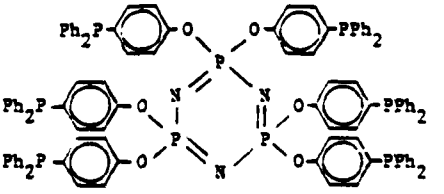


Scheme 2

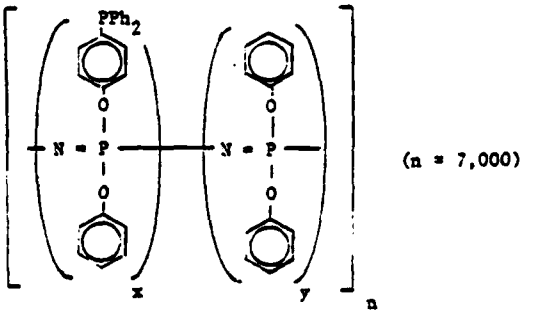
Typical products prepared by this route include XXV, XXVI, and XXVII.



XXV



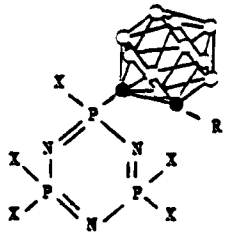
XXVI



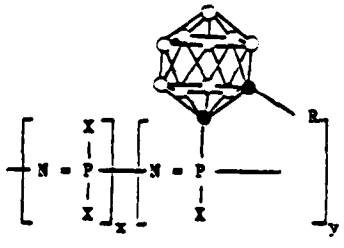
XXVII

Species such as XXV, XXVI, or XXVII readily form coordination complexes when treated with AuCl, $H_2Os_3(CO)_{10}$, $Mn(CO)_3(\eta\text{-}C_5H_5)$, $Fe(CO)_3(PhCH{=}CHC(O)CH_3)$, or $[RhCl(CO)_2]_2$ (25). Two results are of special interest. First, the skeletal nitrogen atoms in XXV-XXVII do not participate in the coordination process. Presumably, they are effectively shielded by the aryloxy units and are of low basicity. Second, coordinative crosslinking can occur when two phosphine residues bind to one metal atom. Ligand-exchange reactions were detected for the rhodium-bound species. The tri-osmium cluster adducts of XXV, XXVI, and XXVII are catalysts for the isomerization of 1-hexane to 2-hexene.

Carboranyl Phosphazenes. Cyclic trimeric and high polymeric chlorophosphazenes react with lithiocarboranes to form carboranyl phosphazenes, as shown in XXVIII and XXIX (28).



XXVIII



XXIX

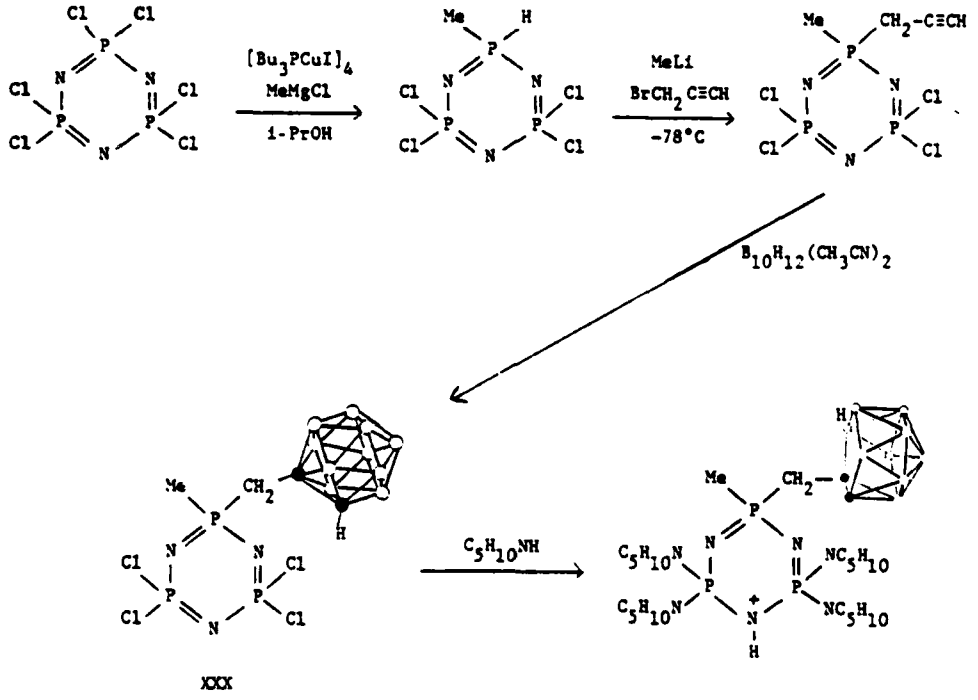
R = Me or Ph, and X = Cl or OCH_2CF_3

(O = BH)

(● = C)

The halogen atoms remaining can then be replaced by organic residues such as trifluoroethoxy units. High polymers can also be prepared by ring-opening polymerization of the chlorocyclophosphazene, XXVIII. Compounds of this type can be converted to nido-carboranes in the presence of base, but these do not form metallo-derivatives, presumably for steric reasons (29).

However, separation of the carborane cage from the phosphazene ring or chain by a methylene spacer group allows metals to be inserted into the open face of the carborane. These syntheses were accomplished by the reaction routes shown in Schemes 3 and 4. High polymeric analogues of these transformations have also been accomplished following polymerization of XXX. The rhodium-bound cyclophosphazenes and polyphosphazenes are catalysts for the hydrogenation of 1-hexene. In this, they show a similar behavior to metallocarboranes linked to polystyrene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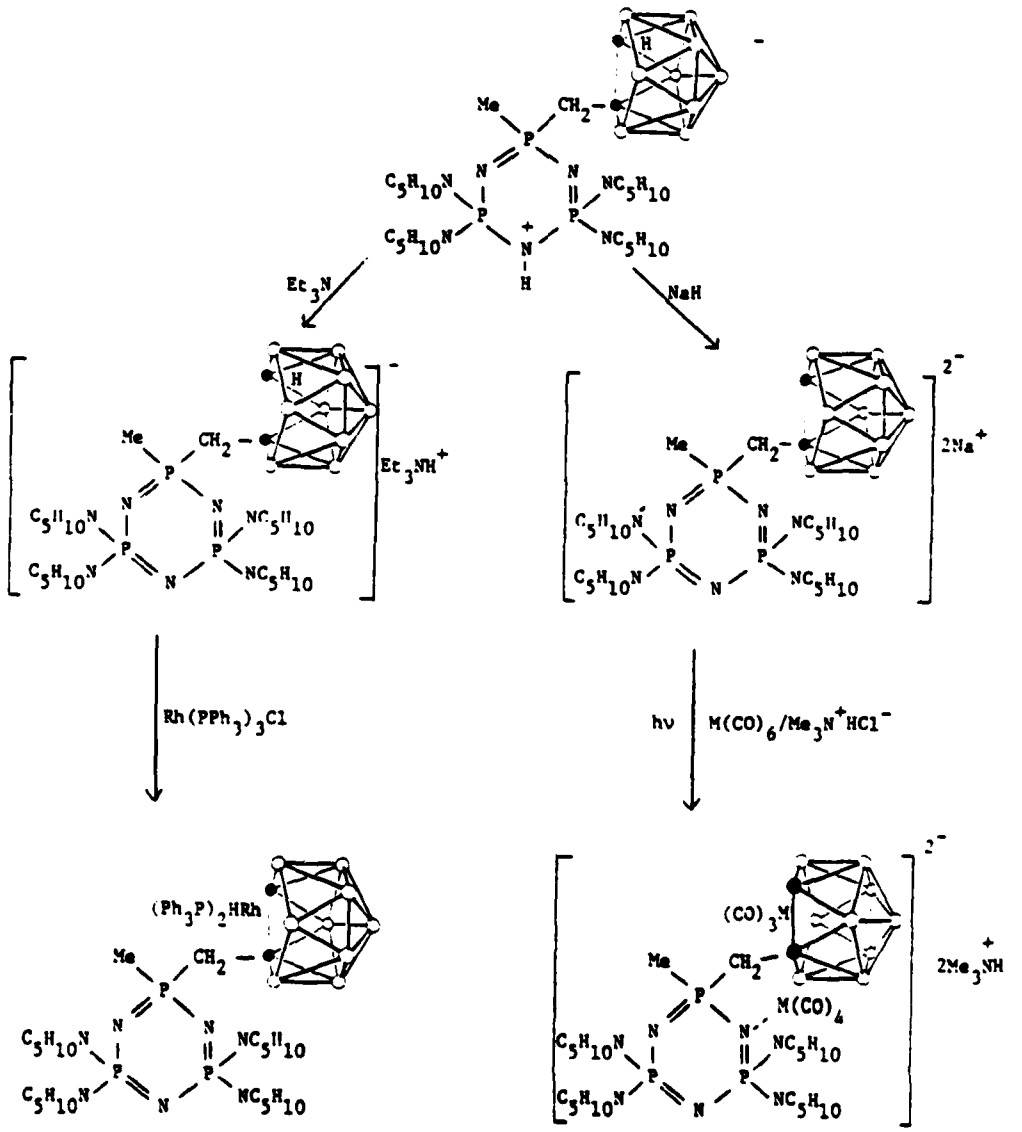
MeMgCl
i-PrOH
MeLi
BrCH2C≡CH
-78°C
B10H12(CH3CN)2
C5H10NH
XXX
O = BH
● = C

Scheme 3

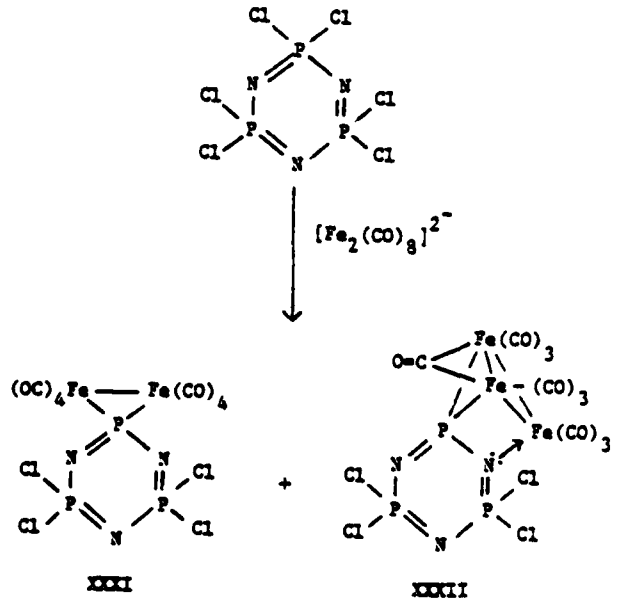


Scheme 4

(34). The oxidative-stability of the phosphazene backbone is expected to be an advantage in catalytic reactions.

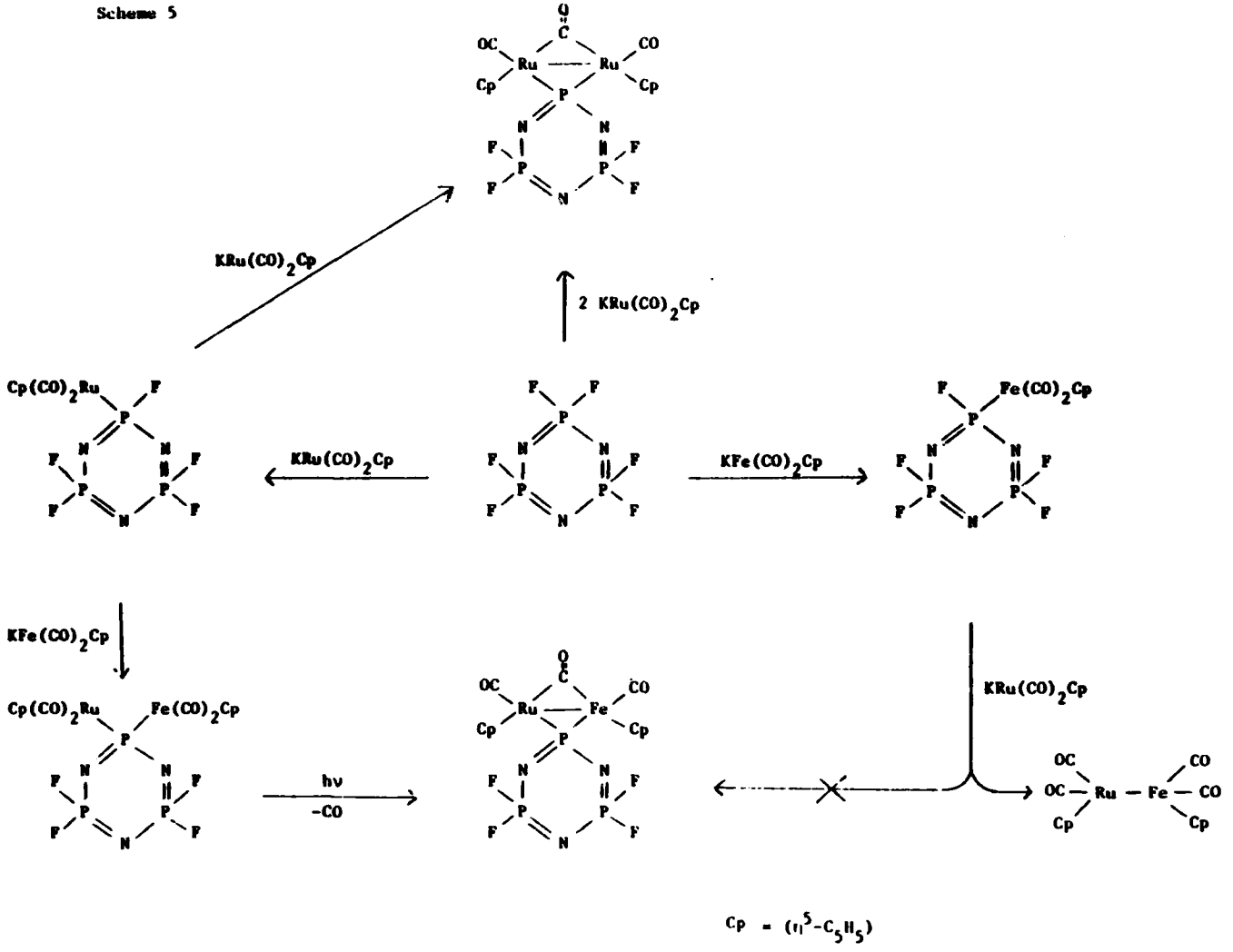
Metallophosphazenes with Phosphorus-Metal Bonds. Until recently, the chemistry of cyclic and high polymeric phosphazenes was essentially the chemistry of their organic derivatives (Scheme 1). However, a discovery reported in 1979 (31) opened up a new field of metallophosphazene chemistry in which transition metals form the nucleus of the side group structure and are linked to the skeleton through phosphorus-metal bonds. These species are of theoretical and potentially practical importance, and I will summarize briefly some of the main features known at this time.

Organometallic anions react with halophosphazenes to replace halogen atoms by organometallic units. The first reactions of this type discovered are illustrated in Scheme 5. The metallophosphazenes are surprisingly stable. Moreover, as shown below, hexachlorocyclotriphosphazene reacts with an organometallic dianion to yield both a dimetallo derivative (XXXI) and a trimetallic cluster derivative (XXXII). The latter compound is



XXXI XXXII

Scheme 5



Cp = (η^5-C_5H_5)

stabilized by both P-metal and N-metal coordinative bonds. Other metallophosphazenes containing Pt and Au have been reported recently by Schmidpeter and coworkers (35). X-ray structure data have been obtained for several of these compounds and, as might be expected, a strong interaction between the metallic units and the phosphazene ring system is evident (31,32,33,36).

Conclusions

The reactions discussed in this chapter are illustrative of the chemical diversity that follows from the substitutive approach to polymer synthesis. Rings and polymers based on the Main Group inorganic elements are especially appropriate for this approach because of the generally high reactivity of, for example, the element-halogen bonds. Thus, a key problem facing the inorganic research community is to devise and develop methods for the synthesis of high polymers, comparable to poly(halophosphazenes), that contain elements such as silicon, aluminum, boron, or sulfur in the skeleton, with reactive side groups attached to these atoms. Once these polymers have been synthesized, a diverse arsenal of side group substitution processes can then be mobilized to prepare a broad range of different macromolecules. If this can be accomplished, it should have an almost unprecedented impact on inorganic chemistry, polymer chemistry, and high technology.

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Figure 1. Traditional and exploratory uses for high polymers. (a) Polymers have been used traditionally for their solid state, chain entanglement behavior which gives rise to strength or elasticity. (b) Polymers used as carrier molecules for bioactive agents are under investigation in controlled-release drug therapy either as targeted macromolecular drugs or as immobilized, biodegradable systems. (c) Transition metal catalysts linked to polymers can be immobilized for ease of manipulation or recovery, or the polymer may modify the catalytic activity. (d) Electrical conduction in polymers may occur along unsaturated chain sequences or between chains in crystalline domains. (e) Sequential arrangement of side groups along a linear polymer chain offers the prospect of control of polymer conformation, or the use of such polymers as templates for the controlled construction of complementary polymer molecules. Such polymers amy also prove useful in the future for information storage at the molecular level.

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